

Exhibit A

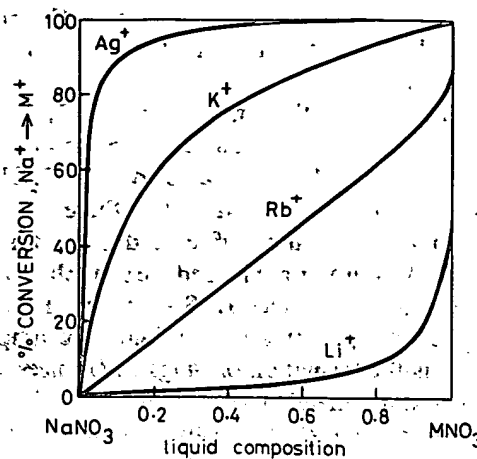


Fig. 2.12 Equilibria between β -alumina and binary nitrate melts at 300 to 350 °C. (From Yao and Kummer, 1967)

shown in Fig. 2.12 for the equilibria between β -alumina crystals and binary nitrate melts containing NaNO_3 and another metal nitrate at 300 to 350 °C. Thus, it is particularly easy to exchange Na^+ for Ag^+ . Also, it is possible to effect a controlled partial ion exchange by controlling the composition of the nitrate melt. Ion-exchanged β -aluminas may also be prepared by electrochemical methods, similar to those described in the preceding section.

Ion exchange reactions have been studied in considerable detail in β -alumina, but the same principles could probably be applied to a wide variety of crystals, especially alkali-containing crystals. Ion exchange reactions are constrained by both kinetic and thermodynamic factors. Kinetic factors are influenced largely by the mobility of ions: at elevated temperatures, e.g. $\sim 300^\circ\text{C}$, alkali ions are often quite mobile in crystals and are capable of ion exchange on immersion in a suitable melt. Thus, $\text{Ag}_2\text{Si}_2\text{O}_5$, which has a silicate sheet structure, has been prepared by immersing $\text{Na}_2\text{Si}_2\text{O}_5$ crystals in molten AgNO_3 at 280 °C. However, it is considerably more difficult to replace or introduce ions with a valency greater than unity since such ions form stronger bonds, whether ionic or covalent, and tend to be immobile. Much higher temperatures may therefore be necessary to effect their ion exchange.

Whereas the rate of ion exchange depends on kinetic factors, the extent of ion exchange, if indeed it occurs at all, depends on thermodynamic factors, as shown in Fig. 2.12 for β -alumina. Ion exchange involves equilibria of ions between the crystal and the melt and, in particular, depends on the activities of the two cations involved in the crystal and in the melt.

2.4.4 Synthesis of new metastable phases by 'Chimie Douce'

The precursor methods described in Sections 2.1.3 and 2.1.4 have the advantage that reaction takes place at much lower temperatures than when using

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